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## Separation of Co(II), Cu(II), Ni(II) and Mn(II) from synthetic hydrochloric acid leaching solution of spent lithium ion batteries by solvent extraction

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**Abstract:** Spent lithium ion batteries contain valuable critical metals such as cobalt, copper, lithium and nickel. In order to develop a process for the separation of the divalent metal ions from spent lithium ion batteries, solvent extraction experiments were performed by employing synthetic hydrochloric acid leaching solution. The synthetic solution contained Cu(II), Co(II), Mn(II) and Ni(II) and its acidity was 3 M HCl. Extraction with Aliquat 336 led to selective extraction of Cu(II) with a small amount of Co(II). After adding NaCl to the Cu(II) free raffinate to enhance the complex formation of Co(II), Co(II) was selectively extracted into Aliquat 336 together with Mn(II). The small amount of Mn(II) in the loaded Aliquat 336 was scrubbed by pure Co(II) solution. After adjusting the pH of the raffinate to 3, 91.3% of Mn(II) was selectively extracted over Ni(II) by the mixture of D2EHPA and Alamine 336. In this extraction, the mole fraction of D2EHPA in the mixture affected the extraction of Mn(II). McCabe-Thiele diagrams for the extraction of Cu(II) and Co(II) were constructed. Batch simulation experiments for the three stage counter-current extraction verified the selective extraction of the target metal ions in each extraction step. Namely, the total extraction percentage of Cu(II) and Co(II) was 71.6% and 98.8% respectively. Most metals in the loaded organic phase were stripped completely with the appropriate agents (1.0 M H<sub>2</sub>SO<sub>4</sub> for Cu(II), 0.1 M H<sub>2</sub>SO<sub>4</sub> for Co(II) and 0.3 M HCl for Mn(II) stripping). A process was proposed to separate the metal ions by solvent extraction.

**Keywords:** spent lithium ion batteries, divalent metal ions, solvent extraction, separation

### 1. Introduction

The use of lithium ion batteries for electronics and high-tech industries has been increasing in recent years due to high power density, long life discharge and recharge capacity (Ordoñez et al., 2016). Although spent lithium ion batteries (LIBs) are dangerous in terms of environment, they contain valuable metals which are needed for the manufacture of advanced materials (Aral and Vecchio-Sadus, 2008; Ordoñez et al., 2016). Among the various processes for the recovery of valuable metals from the LIBs, hydrometallurgical one has some advantages over others on the basis of energy consumption, metal recovery rate and the purity of the recovered metals (Zheng et al., 2018). It has been reported that the leaching of the metals present in the LIBs is significantly affected by the nature of the acid. Among the inorganic acid leaching agents such as HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, HCl led to higher leaching percentage of the metals owing to the chlorine ion's strong tendency to form complexes with metal ions (Xu et al., 2008; Chagnes and Pospiech, 2013; Joulié et al., 2014).

The leaching solution of LIBs by inorganic acid solutions contain metal ions such as Li(I), Cu(II), Co(II), Mn(II), Ni(II), Fe(III) (Wang and Friedrich, 2015; Porvali et al., 2019). The separation and recovery of metal ions from the leaching solution of LIBs are accomplished by combining precipitation and solvent extraction. Firstly, Fe(III) and Mn(II) can be precipitated as Fe(OH)<sub>3</sub> and MnO<sub>2</sub> or Mn<sub>2</sub>O<sub>3</sub> by adding NaOH and KMnO<sub>4</sub> solution, respectively. NaOH and Na<sub>3</sub>PO<sub>3</sub> solutions are added to precipitate

Ni(II) and Li(I) as  $\text{Ni}(\text{OH})_2$  and  $\text{Li}_3\text{PO}_4$ , which can be recovered after filtration and drying. Complete precipitation of Fe(III) and Mn(II) is possible and the recovery percentage of Ni(II) and Li(I) was 99% and 95%, respectively (Chen et al., 2015). However, this method requires multi-step precipitation process and a significant energy consumption due to the control of the reaction temperature and stirring speed. A large amount of caustic soda used for precipitation and for the adjustment of solution pH cause environmental burden. Besides, when pH increases, the co-precipitation of other valuable metals leads to a decrease in the recovery efficiency of these metals. The other disadvantages of precipitation method for the treatment of the leaching solutions of LIBs are the low purity of the recovered metals and the necessity of using lots of water for washing. Therefore, solvent extraction is applied to the separation of the metal ions from the leaching solution of LIBs (Torkaman et al., 2017). The separation of Co(II), Ni(II) and Mn(II) from weak HCl solution can be obtained by solvent extraction with organophosphorus acids such as D2EHPA, PC88A, Cyanex 272, while tertiary amines like trioctylamine (TOA) can be used for the separation of Cu(II) and Co(II) from strong HCl solution (Zhao et al., 2011; Suzuki et al., 2012; Wang et al., 2016; Torkaman et al., 2017; Yao et al., 2018). However, saponification of the organophosphorus acids is necessary to maintain the driving force for the extraction of metal ions from weak acidic solution (Sarangi et al., 1999; Devi et al., 2000; Regel-Rosocka et al., 2016). In the case of tertiary amines, addition of salts containing chloride ion like NaCl is necessary to form complexes of specific metal ions.

It has been reported that a mixture of organophosphorus acid and tertiary amine can suppress the reduction in equilibrium pH by extracting hydrogen ions during extraction from weak acidic solution (Le et al., 2019). Therefore, there is no need to saponify the organophosphorus acids. Moreover, the existence of Cu(II) affects the separation behavior Co(II) and Ni(II) present in the leaching solution of LIBs. In order to develop a process for the recovery of rare metals from the leaching solution of LIBs, solvent extraction experiments were performed by employing commercial extractants like Aliquat 336 and the mixture of D2EHPA and Alamime 336 in this work. For this purpose, a synthetic hydrochloric acid leaching solution of LIBs containing Co(II), Cu(II), Mn(II) and Ni(II), except for Li(I) was employed in this work. The separation of Li(I) is not mentioned for the following reasons: (i) according to previous work Li(I) would not be extracted by commercial extractants from weak acidic solution (Nguyen and Lee, 2018); (ii) Thus, Li(I) can be recovered after separating the divalent metals. The separation behavior of Co(II), Cu(II), Mn(II) and Ni(II) was investigated by varying the concentration of extractants and the acidity of the solution. The extraction and stripping conditions for the separation of Cu(II), Co(II), Mn(II) and Ni(II) were obtained. McCabe-Thiele diagrams for the extraction were constructed and batch simulation experiments for the multi-stage extraction were performed. From the experimental results, a process was proposed for the separation of the metals from the solution.

## 2. Experimental

### 2.1. Reagents and chemicals

Aliquat 336 (ALiCl, 93%) was purchased from BASF Co. and bis-(2-ethylhexyl)phosphoric acid (D2EHPA, 95%) was supported by Cytec Inc. Organic phases were prepared by diluting the extractants with kerosene (Daejung Co., > 90%). Decanol (Daejung Co., > 98%) was added into organic solution (10% v/v) as a modifier to avoid the formation of a third phase when needed.

The composition of the synthetic leaching solution was obtained from the literatures and is shown in Table 1 (Wang and Friedrich, 2015; Porvali et al., 2019). The concentration of HCl in the synthetic solution was adjusted to 3 M. The synthetic solutions were prepared by dissolving corresponding amount of metal chlorides such as  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Junsei Co., > 97%),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Daejung Co., > 97%),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (Daejung Co., > 98%),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Kakuri Co. Kyoto Japan, > 96%) in 3 M HCl solution. Sodium chloride (Jedia Co. Ohio USA, > 99%) was also added to adjust the concentration of chloride ion in the solution. HCl (Dae Jung Chemicals, Korea, 35%) and  $\text{H}_2\text{SO}_4$  (Dae Jung Chemicals, Korea, 95%)

Table 1. The composition of metal ions in the synthetic solution

Metal ions	Cu(II)	Co(II)	Mn(II)	Ni(II)
mg·L <sup>-1</sup>	150.0	938.0	150.0	100.0

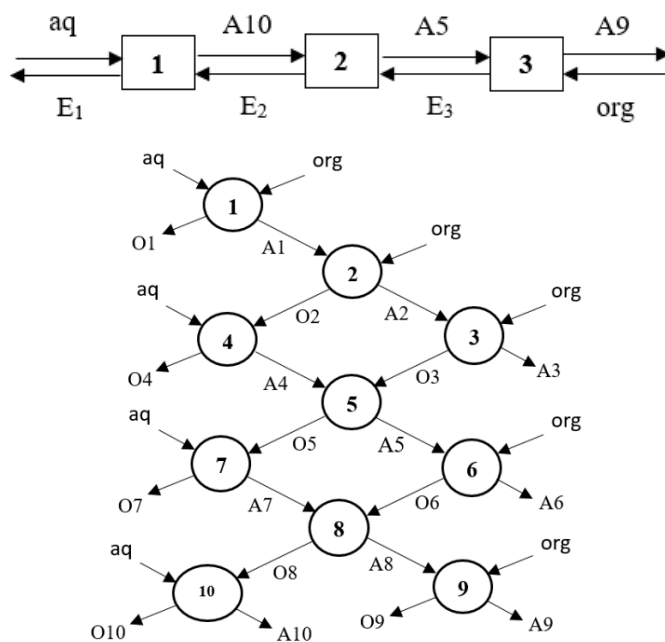
solutions were diluted by doubly distilled water to desirable concentrations. The pH of the solution was adjusted by using HCl solution.

## 2.2. Procedure

The extraction and stripping experiments were performed by mixing equal volume of aqueous and organic phase (each 20 mL) in a screwed cap bottle. When needed, the volume ratio of the two phases was varied. The mixtures were stirred for 30 minutes using a Burrell wrist action shaker (model 75, USA) at ambient temperature ( $22 \pm 1^\circ\text{C}$ ). After shaking, solutions were poured into glass separatory funnel for phase separation. ICP-OES (Inductively coupled plasma-optical emission spectrometry, Spectro Arcos) was used to measure the metal concentration in aqueous phase before and after extraction. The errors associated with the measured concentration of metal ions were within  $\pm 2 \text{ mg}\cdot\text{L}^{-1}$ . Most of the experiments have been done duplicate with an error of  $\pm 5\%$ .

Based on the concentration of the metal ions in the aqueous phase before extraction  $[M]_i$  and after extraction  $[M]_{aq}$ , the extraction percentage (%E) of a metal ion was calculated as:  $\%E = \frac{([M]_i - [M]_{aq}) \times 100}{[M]_i}$ , assuming that there was no volume change of the two phases during the extraction. The stripping percentage of a metal ion was calculated as:  $\%stripping = \frac{[M]_{aq}^* \times 100}{[M]_{org}}$ , where  $[M]_{org}$  and  $[M]_{aq}^*$  are the concentration of a metal ion in the loaded organic phase before stripping and in aqueous phase after stripping, respectively.

Experimental procedure for the batch simulation of the three stage counter-current extraction is shown in scheme 1.



\*Denote: aq = feed solution; org = fresh solvent; A = raffinate; E = extract flow; O = loaded organic phase

Scheme 1. Batch simulation of a three stage counter-current extraction

## 3. Results and discussion

### 3.1 Separation of Cu(II) from solutions containing Co(II), Mn(II) and Ni(II)

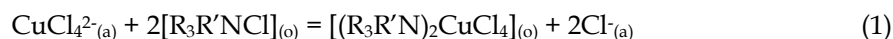
#### 3.1.1. Copper extraction

In HCl solution, metal ions form complexes with chloride ions. The stability constants of the metal ions with chloride ions at  $25^\circ\text{C}$  are listed in Table 2. Among Co(II), Cu(II), Mn(II) and Ni(II), Cu(II) has the strongest tendency to form complexes with chloride ion, while Ni(II) has the weakest. In order to utilize the difference in complex formation tendency among the metals ions, Aliquat 336 with 10% v/v decanol

Table 2. The stability constants of metal complexes in HCl solution at 25°C

Reaction	logK	Reference
$\text{Cu}^{2+} + \text{Cl}^- = \text{CuCl}^+$	0.599	(Uchikoshi and Shinoda, 2018)
$\text{Cu}^{2+} + 2\text{Cl}^- = \text{CuCl}_2^0$	0.343	(Uchikoshi and Shinoda, 2018)
$\text{Cu}^{2+} + 3\text{Cl}^- = \text{CuCl}_3^-$	-1.88	(Uchikoshi and Shinoda, 2018)
$\text{Cu}^{2+} + 4\text{Cl}^- = \text{CuCl}_4^{2-}$	-5.25	(Uchikoshi and Shinoda, 2018)
$\text{Co}^{2+} + \text{Cl}^- = \text{CoCl}^+$	0.22	(Lee and Oh, 2004)
$\text{Co}^{2+} + 2\text{Cl}^- = \text{CoCl}_2^0$	-3.95	(Lee and Oh, 2004)
$\text{Co}^{2+} + 3\text{Cl}^- = \text{CoCl}_3^-$	-3.02	(Lee and Oh, 2004)
$\text{Co}^{2+} + 4\text{Cl}^- = \text{CoCl}_4^{2-}$	-9.06	(Lee and Oh, 2004)
$\text{Mn}^{2+} + \text{Cl}^- = \text{MnCl}^+$	-0.61	(Gammons and Seward, 1996)
$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+$	-1.29	(Rybka and Regel-Rosocka, 2012)

as a modifier was employed for selective extraction of Cu(II) from the solution. Fig. 1 shows that the extraction percentage of Cu(II) increased linearly from 3.1 to 70.5% as Aliquat 336 concentration increased from 0.1 M to 0.5 M. When Aliquat 336 concentration was 0.3 M, Co(II) began to be co-extracted with Cu(II) and 7.6% of Co(II) was extracted by 0.5 M Aliquat 336. Therefore, 0.3 M Aliquat 336 was selected for Cu(II) extraction because the co-extraction of Co(II) was negligible. At this condition, 50% of Cu(II) and 0.7% of Co(II) was extracted into the organic phase, while Mn(II) and Ni(II) were not extracted at all. McCabe-Thiele diagram for the extraction of Cu(II) by 0.3 M Aliquat 336 was constructed by varying the volume ratio of organic to aqueous phase from 1/5 to 5/1. Fig. 2 indicates that 5 stages of counter-current extraction are required for complete extraction of Cu(II) from the solution at an A/O ratio of 1/2. Counter-current extraction can depress the co-extraction of minor elements when the concentration of the extractant is not in excess. Therefore, in order to check the co-extraction of Co(II) with Cu(II), batch simulation experiments on the three stage of counter-current extraction were performed. In these experiments, the phase volume ratio of the two phases was unity and 0.3 M Aliquat 336 was employed. The concentration of the metal ions in each stage and the overall extraction percentage are listed in Table 3. The extraction percentage of Cu(II) was only 71.6% after the three stage of counter-current extraction. However, Co(II), Mn(II) and Ni(II) were not extracted at all, indicating that only Cu(II) can be extracted from the solution. The extraction of Cu(II) from 3 M HCl solution by Aliquat 336 can be represented as (Gammons and Seward, 1996):



where R = C<sub>8</sub> aliphatic and R' = methyl.

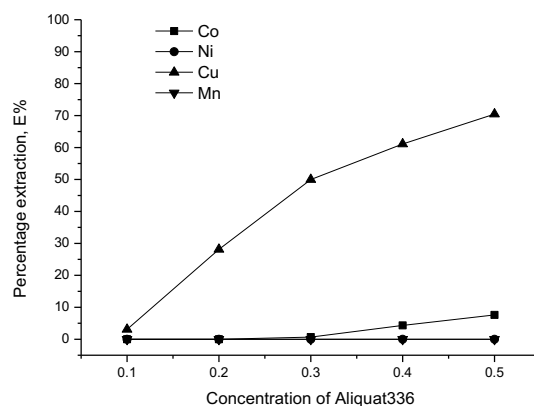


Fig. 1. Effect of Aliquat 336 concentration on the extraction of Cu(II) from 3 M HCl solution

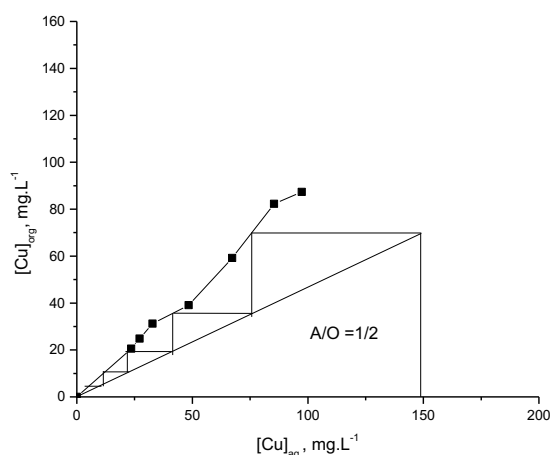


Fig. 2. McCabe Thiele diagram for the extraction of Cu(II) by 0.3 M Aliquat 336 from 3 M HCl solution

Table 3. Results from batch simulation experiments for three stage counter-current extraction by 0.3 M Aliquat 336 at unity phase ratio

Metal ions	Co(II)	Ni(II)	Cu(II)	Mn(II)
Stock solution, mg·L <sup>-1</sup>	938.0	100.0	150.0	150.0
Stage 1, raffinate, mg·L <sup>-1</sup>	916.2	102.5	80.1	149.9
Stage 2, raffinate, mg·L <sup>-1</sup>	972.6	106.1	68.4	156.3
Stage 3, raffinate, mg·L <sup>-1</sup>	938.5	105.3	41.4	155.7
Overall %E	0	0	71.6	0

### 3.1.2. Copper stripping

Previous works (Pospiech and Chagnes, 2015; Torkaman et al., 2017) indicate that strong H<sub>2</sub>SO<sub>4</sub> solution is more effective in stripping Cu(II) from the loaded Aliquat 336 than HCl solution with the same acidity. Therefore, the effect of H<sub>2</sub>SO<sub>4</sub> concentration on the stripping of Cu(II) from the loaded Aliquat 336 was investigated. Experimental results indicated that Cu(II) was completely stripped by H<sub>2</sub>SO<sub>4</sub> solution when its concentration was within 1 to 3 M (O/A = 1).

## 3.2 Separation of Co(II) from the Cu(II) free raffinate

### 3.2.1. Cobalt extraction

After separation of Cu(II) by Aliquat 336, the metals left in raffinate were employed to investigate their separation by preparing a synthetic solution containing Co(II), Mn(II) and Ni(II) (the concentration of metals was 938 mg·L<sup>-1</sup>, 150 mg·L<sup>-1</sup>, and 100 mg·L<sup>-1</sup>, respectively). According to Fig. 1, Aliquat 336 with concentration from 0.4 M can selectively extract Co(II) over Mn(II) and Ni(II). Therefore, the concentration of Aliquat 336 was varied from 0.1 to 1.0 M to investigate Co(II) extraction and the experimental results are shown in Fig. 3. Although Co(II) was selectively extracted over Mn(II) and Ni(II) by Aliquat 336 with 10% (v/v) of decanol, the extraction percentage of Co(II) by 1.0 M Aliquat 336 was less than 20%. This low extraction of Co(II) in our experimental range is due to HCl concentration. Distribution diagram of Co(II) complexes with chloride ion indicates that the mole fraction of anionic complexes of Co(II) at 3 M HCl is low (Lee and Oh, 2004; Lommelen et al., 2019). Therefore, NaCl was added to the solution to enhance the formation of anionic complexes of Co(II). As NaCl concentration increased to 2 M, the extraction percentage of Co(II) increased to 64.6% (see Fig. 4). However, when NaCl concentration was 2 M, 3.5% of Mn(II) was co-extracted into Aliquat 336 together with Co(II). The extraction reaction of Co(II) in presence of large amount of NaCl might be the same as Eq. (1). McCabe-Thiele diagram for the extraction of Co(II) by 1.0 M Aliquat 336 was constructed by varying the volume ratio of the two phases. In these experiments, the concentration of NaCl in the aqueous phase was controlled to 2 M. McCabe Thiele diagram shows that three stages of counter-

current extraction could lead to complete extraction of Co(II) by 1.0 M Aliquat 336 at an A/O ratio of 1/2 (see Fig. 5). Table 4 shows the batch simulation experiments on the three stage of counter-current extraction. Compared to other metal ions, there are some fluctuations in the concentration of Ni(II) in the raffinate of stage 1, 2, and 3. This may be due to analytical error. After three stages of counter-current extraction, the extraction percentage of Co(II) and Mn(II) was 98.8% and 36.9%, while Ni(II) was not extracted at all. In terms of concentration, the concentration of Co(II) and Mn(II) in the loaded Aliquat 336 after 3 stage counter-current extraction was  $392.3 \text{ mg}\cdot\text{L}^{-1}$  and  $26.2 \text{ mg}\cdot\text{L}^{-1}$ , respectively.

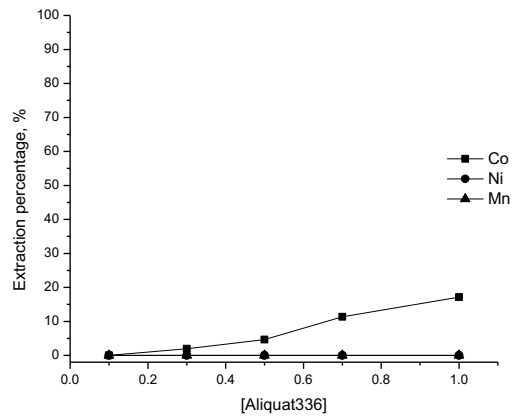


Fig. 3. Effect of Aliquat 336 concentration on the extraction of Co(II) from the Cu(II) free raffinate

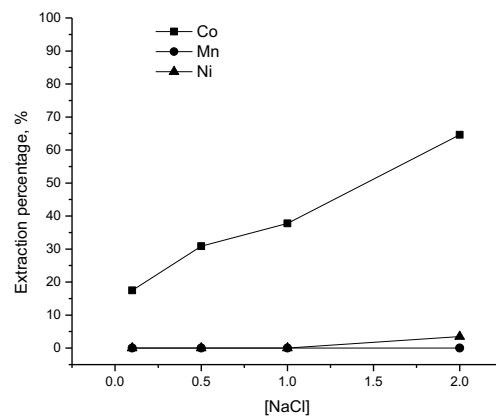


Fig. 4. Effect of NaCl concentration on the extraction of Co(II) from the Cu(II) free raffinate. (organic phase: [Aliquat 336] = 1 M; aqueous phase: 3 M HCl; O/A = 1)

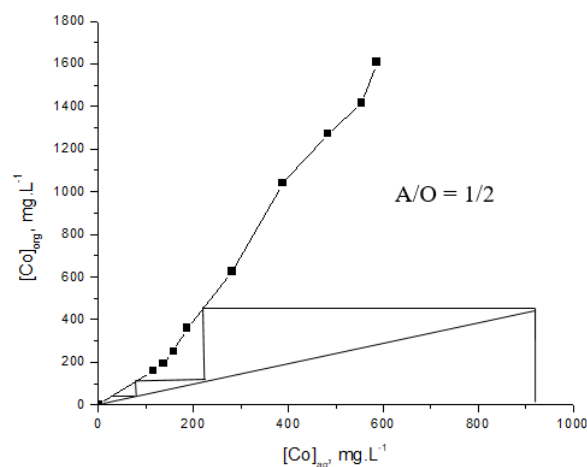


Fig. 5. McCabe Thiele diagram for the extraction of Co(II) by 1.0 M Aliquat 336 from the Cu(II) free raffinate

Table 4. Results from batch simulation experiments for the three stage counter-current extraction of metals by 1.0 M Aliquat 336 from the Cu(II) free raffinate at an O/A ratio of 2

Metal ions	Co(II)	Ni(II)	Mn(II)
Stock solution, mg·L <sup>-1</sup>	938.0	100	150
Stage 1, raffinate, mg·L <sup>-1</sup>	209.0	141.4	124
Stage 2, raffinate, mg·L <sup>-1</sup>	56.1	137.9	120.5
Stage 3, raffinate, mg·L <sup>-1</sup>	12.5	149.7	103.9
Overall % E	98.8	0	36.9

In order to separate the Co(II) and Mn(II) in the loaded Aliquat 336, scrubbing of Mn(II) from the loaded Aliquat 336 was tested by employing pure Co(II) solution. In these experiments, the concentration of Co(II) in the scrubbing solution was varied from 500 to 3000 mg·L<sup>-1</sup> in 3 M HCl and the volume ratio of organic to aqueous phase was fixed at unity. In each scrubbing experiment, the concentration of Co(II) left in the scrubbing solution was calculated by mass balance. Our data indicate that the Mn(II) in the loaded Aliquat 336 was completely scrubbed by the Co(II) solution irrespective of Co(II) concentration in the scrubbing solution. Table 5 lists the scrubbing percentage of Mn(II) and the purity of Co(II) in the scrubbed organic. Based on the data in Table 5, 3 M HCl solution containing 500 mg·L<sup>-1</sup> of Co(II) is recommended for scrubbing. From Table 5, it is observed that some of Co(II) was stripped when the concentration of Co(II) in the scrubbing solution was less than 1000 mg·L<sup>-1</sup>. The concentration of 3 M HCl is not enough to lead to the formation of anionic complexes of Co(II). Therefore, some of Co(II) in the loaded Aliquat 336 was stripped to the scrubbing solution when there is no NaCl in the scrubbing solution. Therefore, the scrubbed Aliquat 336 contained only Co(II), while the scrubbing solution contained both Co(II) and Mn(II). This scrubbing solution containing both metal ions will be returned to the feed solution for further extraction of Co(II).

Table 5. Variation in the scrubbing of Mn(II) from the loaded 1.0 M Aliquat 336 with the concentration of Co(II) in the 3 M HCl solution

Concentration of Co(II) in scrubbing solution (3 M HCl), mg·L <sup>-1</sup>	Concentration of Co(II) and Mn(II) in the organic phase, mg·L <sup>-1</sup>		Scrubbing percentage of Mn(II), %
	Co(II)	Mn(II)	
500	239.7	0	>99.9
1000	388.0	0	>99.9
2000	774.3	0	>99.9
3000	1175.3	0	>99.9

\*The concentration of Co(II) and Mn(II) in the loaded 1.0 M Aliquat 336 before scrubbing was 392.3 and 26.2 mg·L<sup>-1</sup>, respectively.

### 3.2.2. Cobalt stripping

After scrubbing of Mn(II), Co(II) in the scrubbed Aliquat 336 was stripped with H<sub>2</sub>SO<sub>4</sub> solution. In these experiments, the concentration of H<sub>2</sub>SO<sub>4</sub> was varied from 0.1 M to 1.0 M and the volume ratio of the two phases was unity. Our data indicates that Co(II) was completely stripped from the Aliquat 336 irrespective of H<sub>2</sub>SO<sub>4</sub> concentration.

### 3.3. Separation of Mn(II) from the raffinate

#### 3.3.1. Mn(II) extraction

The previous data indicated that it was difficult to extract Mn(II) from 3 M HCl solution by Aliquat 336. Several extraction data have been reported on the separation of Mn(II) and Ni(II) from weak acidic solution by using organophosphorous acids (Hoh et al., 1984; Zhang and Cheng, 2007; Devi, 2015). According to these data, extraction with D2EHPA could selectively extract Mn(II) over Ni(II) from weak

acidic solution. However, it is necessary to control the equilibrium pH of the aqueous phase to obtain high extraction percentage of Mn(II). In general, saponification of organophosphorus acids is employed for the control of equilibrium pH. However, the cost related to saponification is high and some environmental problems may result. Therefore, the mixture of D2EHPA and Alamine 336 was employed in this work for the selective extraction of Mn(II). For this purpose, the effect of mole fraction of D2EHPA and total concentration of the mixture was investigated. The mole fraction of D2EHPA was varied from 0.2 to 1.0 and the total concentration of the mixture was varied from 0.5 M to 2.0 M in kerosene with 10% decanol as a modifier. In these experiments, the raffinate contains  $150 \text{ mg}\cdot\text{L}^{-1}$  Mn (II),  $100 \text{ mg}\cdot\text{L}^{-1}$  Ni(II), and 2.0 M NaCl. According to some previous reports (Hoh et al., 1984; Zhang and Cheng, 2007; Devi, 2015), D2EHPA can extract well Mn(II) around pH of 3.0. Thus, the initial pH of the aqueous phase was adjusted to 2.95.

Fig. 6 shows the influence of mole fraction of D2EHPA in the mixture on the extraction of Mn(II) and Ni(II). When the mole fraction of D2EHPA in the mixture was less than 0.6, the extraction of Mn(II) was negligible. About 35% of Mn(II) was extracted into 0.5 M of the mixture of D2EHPA and Alamine 336 when the mole fraction of D2EHPA was 0.8. Thus, this mole fraction of D2EHPA in the mixture (0.8) was selected for further experiments.

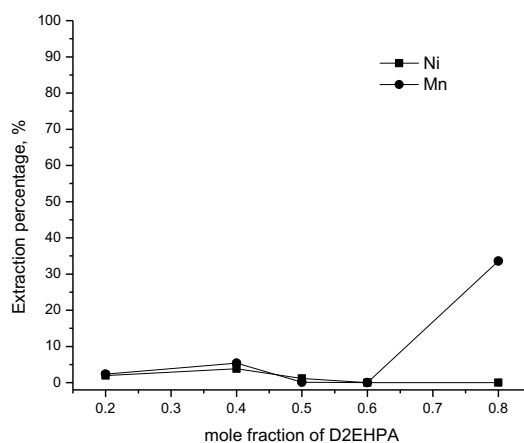
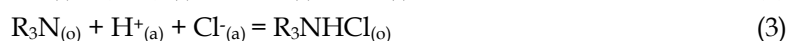
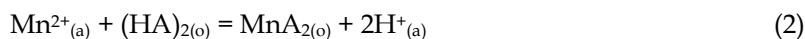


Fig. 6. Effect of mole fraction of D2EHPA in the mixture on the extraction of Mn(II) and Ni(II) from solution with pH 2.95. (The concentration of D2EHPA and Alamine 336 in the mixture was fixed at 0.5 M and 10% decanol was present as a modifier)

Fig. 7 shows the effect of the total concentration of the mixture of D2EHPA and Alamine 336. In these experiments, the mole fraction of D2EHPA in the mixture was fixed at 0.8. The extraction percentage of Mn(II) significantly increased from 33.6 to 91.3% as the total concentration of the mixture was increased from 0.5 to 2.0 M. In these experimental ranges, the extraction percentage of Ni(II) increased from 5.4 to 7.8%. Employment of counter-current extraction can suppress the co-extraction of Ni(II) by the mixture of D2EHPA and Alamine 336.

The equilibrium pH of the raffinate after extraction with 2.0 M mixture was 2.1. The less decrease in the equilibrium pH showed the effect of Alamine 336 in the mixture as an extractant for hydrogen ions during the extraction (Hoh et al., 1984; Le et al., 2019). The extraction reaction of Mn(II) by the mixture of D2EHPA and Alamine 336 can be represented as



where HA and  $\text{R}_3\text{N}$  are D2EHPA and Alamine 336, respectively.

### 3.3.2. Mn(II) stripping

Stripping of Mn(II) from the loaded mixture of D2EHPA and Alamine 336 was investigated by employing HCl and  $\text{H}_2\text{SO}_4$  solution. In these experiments, the concentration of both acids was varied from 0.1 to 0.5 M. There was not much difference in the stripping percentage of Mn(II) with HCl and



H<sub>2</sub>SO<sub>4</sub> solution (see Table 6). It is possible to completely strip Mn(II) from the loaded mixture by using 0.3 M HCl as a stripping solution.

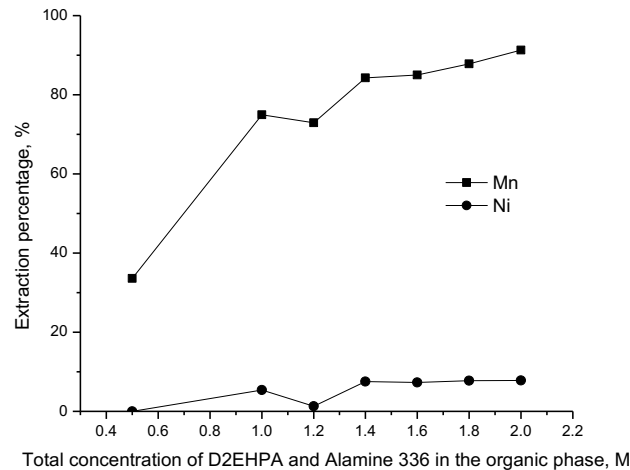


Fig. 7. Effect of the total concentration of the mixture of D2EHPA and Alamine 336 on the extraction of Mn(II) and Ni(II) from the solution with pH 2.95. (The mole fraction of D2EHPA in the mixture was fixed at 0.8)

Table 6. Stripping percentage of Mn(II) from the loaded phase mixture of D2EHPA and Alamine 336 by HCl and H<sub>2</sub>SO<sub>4</sub> solution

Concentration (M)	Stripping percentage (%)	
	HCl	H <sub>2</sub> SO <sub>4</sub>
0.1	97.1	99.2
0.3	100.0	100.0
0.5	99.6	95.3

### 3.4. Integrated procedure

Fig. 8 displays the proposed process for the separation of Cu(II), Co(II), Mn(II) and Ni(II) from the synthetic 3.0 M HCl leaching solution of LIBs. Firstly, Cu(II) can be selectively extracted by using low concentration of Aliquat 336. The Cu(II) in the loaded Aliquat 336 can be stripped by moderate H<sub>2</sub>SO<sub>4</sub>

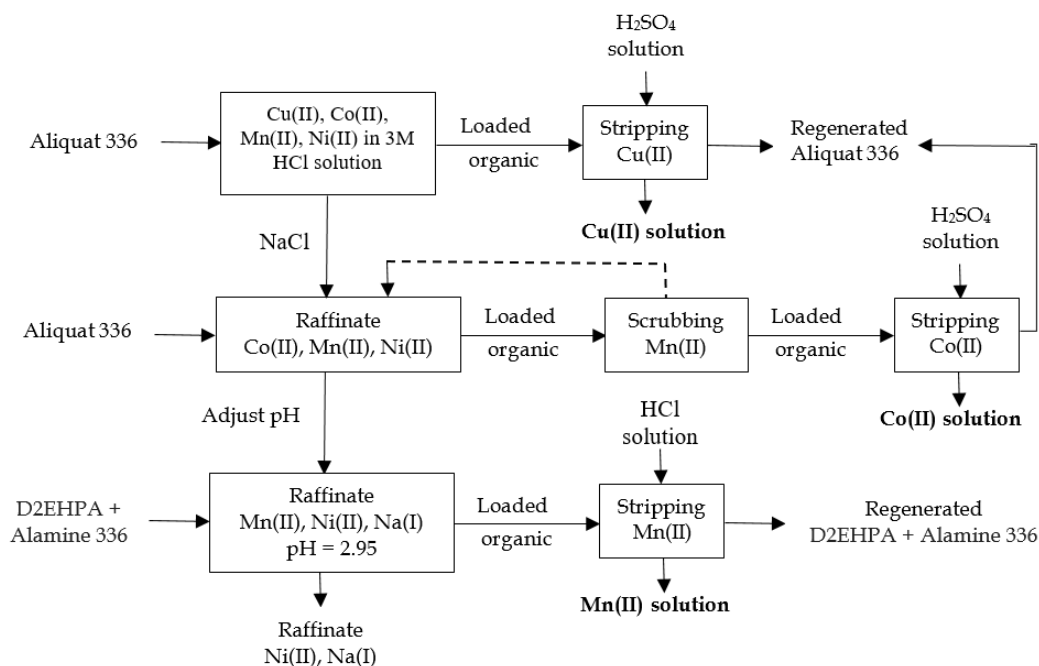


Fig. 8. Integrated process for the separation of Cu(II), Co(II), Mn(II), and Ni(II) from 3 M HCl solution

solution. After adding NaCl to the raffinate, most of Co(II) and a small amount of Mn(II) would be extracted into Aliquat 336. The Mn(II) in the loaded Aliquat 336 can be scrubbed by 3 M HCl solution containing Co(II). The solution containing Co(II) and Mn(II) after scrubbing will be returned to the feed solution for further extraction (see Fig. 8). After adjusting the pH of the raffinate to around 3.0, Mn(II) can be selectively extracted by the mixture of D2EHPA and Alamine 336 where the mole fraction of D2EHPA is 0.8. The Mn(II) in the loaded mixture can be stripped by HCl solution.

The advantage of this process is that the separation of metal ions from HCl leaching solution of LIBs can be obtained by using commercial extractants. A simple solvent extraction process can separate valuable metals. Under the proposed process, Li(I) ion in the real leaching solution of LIBs would remain with Ni(II) in the raffinate after the extraction of Cu(II), Co(II) and Mn(II) by Aliquat 336 and the mixture of D2EHPA and Alamine 336. Moreover, the use of the mixture of D2EHPA and Alamine 336 would avoid the saponification of organophosphorous extractants for the control of the equilibrium pH. However, addition of chloride ion is necessary to promote the separation of Co(II) from the Cu(II) free raffinate. Control of the acidity of the solution is also needed to separate Mn(II) and Ni(II) from the Co(II) free raffinate. More work should be done to get the details in each extraction and stripping step with real leaching solution of LIBs. Table 7 presents the summary on the extraction and stripping percentage of metals from synthetic solution of 3 M HCl.

Table 7. Summary on the extraction and stripping percentage of metals from synthetic solution

Process	Detail	Cu(II)	Co(II)	Mn(II)	Ni(II)
Feed solution	Synthetic leaching solution, 3 M HCl, mg·L <sup>-1</sup>	150.0	938.0	150.0	100.0
Cu(II) separation	Extraction: 0.3 M Aliquat 336, O/A = 1 with three stage counter-current extraction, %	71.6	0	0	0
	Stripping: 1 M H <sub>2</sub> SO <sub>4</sub> , A/O = 1, %	>99.9	-	-	-
Co(II) separation	Extraction: 1.0 M Aliquat 336, O/A = 2 with three stage counter-current extraction, %	-	98.8	36.9	0
	Scrubbing: 500 mg·L <sup>-1</sup> Co(II) in 3 M HCl, %	-	-	>99.9	-
	Stripping: 0.1 M H <sub>2</sub> SO <sub>4</sub> , O/A = 1, %	-	>99.9	-	-
Mn(II) separation	Extraction: 2 M mixture of Alamine 336 and D2EHPA, O/A = 1, %	-	-	91.3	7.8
	Stripping: 0.3 M HCl, %	-	-	>99.9	-
Ni(II) in raffinate	Final raffinate, mg·L <sup>-1</sup>	-	-	-	92.2

\*Note: 2 M Na(I) remains in final raffinate

#### 4. Conclusions

Solvent extraction experiments were performed to separate the metal ions from the hydrochloric acid leaching solutions of spent lithium ion batteries. In this work, a synthetic solution containing Co(II), Cu(II), Ni(II), and Mn(II) was employed for the experiment and its acidity was adjusted to 3 M HCl. Selective extraction of Cu(II) over other metal ions was possible by employing 0.3 M Aliquat 336. Batch simulation experiments for the three stage counter-current extraction with Aliquat 336 verifies that only Cu(II) was extracted, leaving the other metal ions in the raffinate. Namely, after the three stage counter-current extraction 71.6% of Cu(II) was extracted. Subsequently, 98.8% of Co(II) was selectively extracted together with a small amount of Mn(II) by 1.0 M Aliquat 336 after adding 2 M NaCl to the Cu(II) free raffinate (with the three stage counter-current extraction). The co-extracted Mn(II) was successfully scrubbed by pure Co(II) solution with 3 M HCl. Batch simulation experiments on the three stage counter-current extraction verified that no Ni(II) was extracted at this condition. The Cu(II) and Co(II) in the loaded organic were completely stripped by H<sub>2</sub>SO<sub>4</sub> solution. After adjusting the pH of the raffinate to around 3, employment of the mixture of D2EHPA and Alamine 336 selectively extracted 91.3% of Mn(II) over Ni(II). The Mn(II) in the loaded mixture was stripped by HCl solution. The mole

fraction of D2EHPA in the mixture and the total concentration significantly affected the extraction of Mn(II). McCabe-Thiele diagrams for the extraction of Cu(II) and Co(II) were constructed. A process was proposed to separate the 4 metal ions by solvent extraction on the basis of our data.

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